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(54) [Title of the Invention]

A working fluid mixture

(57) [Abstract]

[Constitution] A working fluid mixture which is characterized in that the indispensable components are difluoromethane, trifluoroethane, tetrafluoroethane and pentafluoroethane.

[Effects] The present invention has outstanding performance as a replacement medium for R-502 which is used in particular in low temperature fields, and there is obtained the same performance as R-502 without major equipment modification. Furthermore, since the indispensable components are hydrofluorocarbons, there is no damage to the ozone layer.

[Scope of Claims]

[Claim 1] A working fluid mixture which is characterized in that the indispensable components are difluoromethane, trifluoroethane, tetrafluoroethane and pentafluoroethane.

[Claim 2] A working fluid mixture according to Claim 1 where the mixing proportions of the difluoromethane, trifluoroethane, tetrafluoroethane and pentafluoroethane are difluoromethane/trifluoroethane/tetrafluoroethane/pentafluoroethane = 3-40 wt%/5-60 wt%/5-60 wt%/10-87 wt%.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application] The present invention relates to a working fluid mixture for use in, for example, air conditioners, freezers, heat pumps and the like.

[0002]

[Prior-Art] In recent years, attention has been focussed on the environmental problem of ozone layer damage due to the effects of chlorofluorocarbons (hereinafter abbreviated to CFCs) and a total phasing-out of these by the end of 1995 has been decided. Furthermore, there is also a trend towards eventually phasing-out hydrochlorofluorocarbons (hereinafter abbreviated to HCFCs) which have a lesser effect in terms of ozone layer damage. Hence, there is a demand for the rapid development of replacements for these CFCs and HCFCs. In particular, there is a pressing need for the development of a medium which can replace the azeotropic mixed refrigerant (hereinafter referred to as R-502) of 48.8 wt% difluorochloromethane (hereinafter referred to as HCFC-22) and 51.2 wt% pentafluoromonochloroethane (hereinafter referred to as CFC-115), which is used in low temperature equipment.

[0003]

[Problem to be Overcome by the Invention] The present invention has as its main objective to provide a working fluid mixture which has an ozone layer depletion potential of zero, has outstanding performance as a

refrigerant and can be used without major equipment modification.

[0004] Hitherto, a number of candidate media have been developed but it cannot be said that they have satisfactory performance. For example, in JP-A-1-108291, a mixture of trifluoroethane and pentafluoroethane is disclosed. This mixed medium has outstanding refrigerant performance but it has the disadvantage solely that its coefficient of performance is poor.

[0005] Furthermore, in JP-A-6-170585, there is disclosed a three-component mixed refrigerant of difluoromethane, tetrafluoromethane and pentafluoroethane. With this mixed refrigerant, it is possible to obtain a composition of outstanding refrigerating capacity and coefficient of performance but, since the discharge pressure is extremely high, it is necessary to increase the equipment strength. Moreover, there is the disadvantage that it is highly non-azeotropic, and the temperature gradient within a heat exchanger is extremely high so considerable modification to existing equipment is required.

[0006] On the other hand, in JP-A-3-170588 there is disclosed a mixed medium of trifluoroethane, tetrafluoroethane and pentafluoroethane. This mixed medium satisfies target performance values in terms of refrigerating capacity, discharge pressure and discharge temperature but has the disadvantage solely that its coefficient of performance is poor.

[0007] Again, in JP-A-5-70769 there is disclosed a mixed medium of difluromethane and 1,1,1-trifluoroethane. This mixed medium has components which both fall within the

flammability range so there is a considerable problem from the point of view of safety. In addition, there is the disadvantage that the higher the proportion of the difluoromethane the greater is the compressor discharge temperature. Thus, as stated above, the two-component and three-component mixed media proposed hitherto cannot be said to have totally satisfactory performance in terms of all the properties required of a replacement for R-502.

[0008]

[Means for Resolving the Problem] As a result of considerable research against this technical background, it has been discovered that a working fluid mixture which is characterized in that the indispensable components are the hydrofluorocarbons (hereinafter abbreviated to HFCs) difluoromethane (referred to below as HFC-32), trifluoroethane, tetrafluoroethane and pentafluoroethane (referred to below as HFC-125) possesses the requisites for meeting the objectives of the present invention.

[0009] If the proportion of the HFC-32 is too high, there are the disadvantages that the compressor discharge pressure and discharge temperature are raised and, furthermore, there is the danger of the mixture becoming flammable. On the other hand, if the proportion of the HFC-32 is too low, then there is the disadvantage that a high coefficient of performance and a high refrigerating capacity are not obtained. Consequently, the proportion of HFC-32 in the mixture of HFC-32, trifluoroethane, tetrafluoroethane and HFC-125 (referred to below as mixture A) is 3 to 40 wt%, and preferably 10 to 20 wt%.

[0010] If the proportion of the trifluoroethane in mixture A exceeds 60 wt%, there is a danger of flammability, whereas with too little there is the disadvantage that performance falls. Hence, the proportion of the trifluoroethane is 5 to 60 wt% and in particular 15 to 40 wt%.

[0011] When the proportion of the tetrafluoroethane in mixture A is raised, the coefficient of performance increases but there is the disadvantage that the refrigerating capacity is reduced. As a result of an investigation taking into account the compressor discharge pressure and discharge temperature characteristics, the preferred amount thereof is 5 to 60 wt% and in particular 15 to 40 wt%.

[0012] The pentafluoroethane in mixture A has the effect of suppressing the flammability of the difluoromethane and trifluoroethane. The actual proportion thereof in the mixture will be determined by the composition of the other three components but, in particular, it will lie in the range 10 to 87 wt%, and preferably 25 to 60 wt%.

[0013] With regard to the tetrafluoroethane in the present invention, two isomers are known, namely 1,1,2,2-tetrafluoroethane (hereinafter referred to as HFC-134) and 1,1,1,2-tetrafluoroethane (hereinafter referred to as HFC-134a) but their properties are similar, so these may be used on their own or they may be used as mixtures.

[0014] Furthermore, two isomers of trifluoroethane are known, namely 1,1,1-trifluoroethane (hereinafter referred to as HFC-143a) and 1,1,2-trifluoroethane (hereinafter referred to as HFC-143). In terms of the objectives of

the present invention, HFC-143a, which has a standard boiling point value of about -47°C, is superior, but there can also be used HFC-143a containing the isomer HFC-143.

[0015] The working fluid of the present invention is effective for application to a refrigeration cycle used for the purposes of refrigeration, freezing or air conditioning in the low-medium temperature and high temperature fields, but it can also be used as a working fluid for a Rankin cycle or for various other heat-recovery techniques.

[0016] The working fluid mixture of the present invention is outstanding in its thermal stability and it does not require a stabilizer under normally-employed conditions. However, in cases where the thermal stability needs to be raised for use under severe conditions, there can be incorporated a stabilizer such as propylene oxide, 1,2-butylene oxide, glycidol or other epoxide, dimethyl phosphite, diisopropyl phosphite, diphenyl phosphite or other such phosphite, trilauryl trithiophosphite or other such thiophosphite, triphenoxyphosphine sulphide, trimethylphosphine sulphide or other such phosphine sulphide, boric acid, triethyl borate, triphenyl borate, phenylboronic acid, diphenylboronic acid or other such boron compound, 2,6-di-t-butyl-p-cresol or other such phenol, nitromethane, nitroethane or other such nitro-alkane, methyl acrylate, ethyl acrylate or other such acrylate ester, or dioxane, tert-butanol, pentaerythritol, p-isopropenyltoluene or the like, in an amount lying within the range 0.001 to 10 parts by weight and preferably 0.01 to 5 parts by weight per 100 parts by weight of the working fluid mixture.

[0017] Moreover, there may also be incorporated into the working fluid mixture of the present invention, in an amount lying within the range such that the objectives of the invention are not impaired, compounds like HFCs other than those in mixture A such as trifluoromethane and 1,1-difluoroethane, ethers such as dimethyl ether, pentafluoro-ether and perfluorodimethyl ether, amines such as perfluoroethylamine and perfluorodimethylamine, hydrocarbons such as propane and butane, and perfluoro-compounds such as perfluoroethane and perfluoropropane.

[0018]

[Examples]

[Examples 1 to 7, Comparative Examples 1 to 5] A 1 horsepower freezer filled with a working fluid mixture of composition shown in Table 1 was operated with the vaporization temperature of the refrigerant in the evaporator at -30°C, the condensation temperature of the refrigerant in the condenser at 40°C, the degree of superheating at the compressor inlet = 0°C and the degree of supercooling at the expansion valve inlet = 0°C. A polyalkylene glycol oil was used as the freezer oil. As a result, the coefficient of performance (COP), the refrigerating capacity, the compressor discharge pressure, the compressor discharge temperature and the temperature difference at the condenser inlet/outlet were as shown in Table 2.

[0019] As can be seen from Examples 1 to 6, with the working fluid mixture of the present invention the coefficient of performance and the refrigerating capacity

are the same as for R-502, and the increase in the compressor discharge pressure and discharge temperature are, at most, only 300 kPa and 8°C respectively. Furthermore, the heat-exchanger internal temperature difference (the temperature difference at the condenser inlet/outlet) is at most 4°C. Thus, it is a working fluid mixture where non-azeotropy is suppressed, and it is clear that at least as good a performance is shown as R-502 without marked modification to the conventional equipment.

[0020] On the other hand, in the case of the two-component mixed medium comprising HFC-143a/HFC-125 shown in Comparative Example 1, and the three-component mixed medium comprising HFC-143a/HFC-134a/HFC-125 shown in Comparative Example 3, there is the disadvantage of a low coefficient of performance. Again, in the case of the two-component mixed medium comprising HFC-32/HFC-125 shown in Comparative Example 2, while the coefficient of performance and the refrigerating capacity are outstanding, there is a considerable rise in the compressor discharge pressure and discharge temperature, so there is the disadvantage that considerable improvement to the equipment is required, which is impractical. Moreover, in the case of the three-component mixed medium comprising HFC-32/HFC-134a/HFC-125 shown in Comparative Example 4, while the coefficient of performance is outstanding, there is the disadvantage of a high compressor discharge temperature and high heat-exchanger internal temperature difference.

[0021]

[Table 1]

	HFC-32 [wt%]	HFC-143a [wt%]	HFC-134a [wt%]	HFC-125 [wt%]
Example 1	5	50	5	40
Example 2	7	30	15	48
Example 3	7	40	15	38
Example 4	10	30	10	50
Example 5	10	35	20	35
Example 6	20	20	15	45
Comp.Ex.1	0	50	0	50
Comp.Ex.2	50	0	0	50
Comp.Ex.3	0	52	4	44
Comp.Ex.4	23	0	52	25

[0022]

[Table 2]

	COP	Refrigerating capacity	Compressor Discharge Pressure kPa	Compressor Discharge Temperature °C	Condenser Inlet/Outlet Temperature Difference °C
Example 1	0.97	1.04	200	-2	1
Example 2	0.98	1.00	150	-1	2
Example 3	0.98	1.01	140	0	2
Example 4	0.98	1.03	190	1	2
Example 5	1.00	1.01	120	2	2
Example 6	1.00	1.14	300	7	2
Comp.Ex.1	0.93	1.00	200	-6	0
Comp.Ex.2	1.00	1.54	740	23	0
Comp.Ex.3	0.94	0.98	150	-5	1
Comp.Ex.4	1.06	0.99	-30	13	5
COP and refrigerating capacity expressed as a comparison with R-502 compressor discharge pressure expressed as the difference from that of R-502 compressor outlet temperature expressed as the difference from that of R-502					

[0023]

[Effects of the Invention] The present invention has outstanding performance as a replacement medium for R-502 which is used in particular in low temperature fields,